



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification 6 : C08F 4/60, 10/00, 110/02, 110/06, 110/14, 210/02, 210/06, 210/14, 23/16, C09J 123/00, C10M 119/00, C09D 123/00, C08J 5/18, C08F 32/04, 214/18, 220/22, C08G 61/04, C07C 251/00</p>	<p>A3</p>	<p>(11) International Publication Number: WO 96/23010</p> <p>(43) International Publication Date: 1 August 1996 (01.08.96)</p>															
<p>(21) International Application Number: PCT/US96/01282</p> <p>(22) International Filing Date: 24 January 1996 (24.01.96)</p> <p>(30) Priority Data:</p> <table border="0"> <tr> <td>08/378,044</td> <td>24 January 1995 (24.01.95)</td> <td>US</td> </tr> <tr> <td>08/415,283</td> <td>3 April 1995 (03.04.95)</td> <td>US</td> </tr> <tr> <td>08/473,590</td> <td>7 June 1995 (07.06.95)</td> <td>US</td> </tr> <tr> <td>60/007,375</td> <td>8 August 1995 (08.08.95)</td> <td>US</td> </tr> <tr> <td>60/002,654</td> <td>22 August 1995 (22.08.95)</td> <td>US</td> </tr> </table> <p>(71) Applicants: E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). UNIVERSITY OF NORTH CAROLINA AT CHAPEL HILL [US/US]; Office of Technology Development, Campus Box 4105, 308 Bynum Hall, Chapel Hill, NC 27599-4105 (US).</p> <p>(72) Inventors: JOHNSON, Lynda, Kaye; Apartment 5B2, 402 Foulk Road, Wilmington, DE 19803-3805 (US). KILLIAN, Christopher, Moore; 406 Summerwalk Circle, Chapel Hill, NC 27514 (US). ARTHUR, Samuel, David; 3214 North Monroe Street, Wilmington, DE 19802-2654 (US). FELDMAN, Jerald; 16 Cinamon Drive, Hockessin, DE 19707-1349 (US). McCORD, Elizabeth, Forrester; 514 Hemlock Drive, Hockessin, DE 19707-9361 (US). McLAIN, Stephan, James; 202 Old Mill Lane, Wilmington, DE 19803-4922 (US). KREUTZER, Kristina, Ann; Apartment 2C, 4 Doe Run Court, Wilmington, DE 19808-2059 (US). BENNETT, Margaret, Anne; 1 Brandywine Falls, Wilmington, DE 19806 (US). COUGHLIN, Edward, Bryan; Apartment E, 2227 Prior Road, Wilmington, DE 19809 (US). ITTEL, Steven, Dale; 2802 Landon Drive, Wilmington, DE 19810-2213 (US). PARTHASARATHY, Anju; 1562 Pottstown Pike, Glenmoore, PA 19343-9614 (US). TEMPEL, Daniel, Joseph; Apartment 10, 400 Davie Road, Carrboro, NC 27510 (US). BROOKHART, Maurice, S.; 944 Old Orchard Road, Chapel Hill, NC 27514 (US).</p>		08/378,044	24 January 1995 (24.01.95)	US	08/415,283	3 April 1995 (03.04.95)	US	08/473,590	7 June 1995 (07.06.95)	US	60/007,375	8 August 1995 (08.08.95)	US	60/002,654	22 August 1995 (22.08.95)	US	<p>(74) Agents: EVANS, Craig, H. et al.; E.I. du Pont de Nemours and Company, Legal Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).</p> <p>(81) Designated States: AL, AM, AU, BB, BG, BR, CA, CN, CZ, EE, FI, GE, HU, IS, JP, KP, KR, LK, LR, LT, LV, MD, MG, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, TR, TT, UA, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AZ, BY, KG, KZ, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p>Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p> <p>(88) Date of publication of the international search report: 5 December 1996 (05.12.96)</p>
08/378,044	24 January 1995 (24.01.95)	US															
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60/002,654	22 August 1995 (22.08.95)	US															
<p>(54) Title: α-OLEFINS AND OLEFIN POLYMERS AND PROCESSES THEREFOR</p> <p>(57) Abstract</p> <p>Disclosed herein are processes for polymerizing ethylene, acyclic olefins, and/or selected cyclic olefins, and optionally selected olefinic esters or carboxylic acids, and other monomers. The polymerizations are catalysed by selected transition metal compounds, and sometimes other co-catalysts. Since some of the polymerizations exhibit some characteristics of living polymerizations, block copolymers can be readily made. Many of the polymers produced are often novel, particularly in regard to their microstructure, which gives some of them unusual properties. Numerous novel catalysts are disclosed, as well as some novel processes for making them. The polymers made are useful as elastomers, molding resins, in adhesives, etc. Also described herein is the synthesis of linear α-olefins by the oligomerization of ethylene using as a catalyst system a combination of a nickel compound having a selected α-diimine ligand and a selected Lewis or Bronsted acid, or by contacting selected δ(a)-diimine nickel complexes with ethylene.</p>																	

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INTERNATIONAL SEARCH REPORT

Intern. Application No

PCT/US 96/01282

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08F4/60 C08F10/00 C08F110/02 C08F110/06 C08F110/14
 C08F210/02 C08F210/06 C08F210/14 C08L23/16 C09J123/00
 C10M119/00 C09D123/00 C08J5/18 C08F32/04 C08F214/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08F C08L C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 93 13140 A (EXXON CHEMICAL PATENTS INC) 8 July 1993	1-6,332, 333,358, 359,366, 384-415, 420-438, 539-554, 560-562
	see table II	
A	EP 0 446 013 A (TOSOH CORP) 11 September 1991	1-6,332, 333,358, 359,366, 384-415, 420-438, 539-554, 560-562
	see the whole document	



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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Date of the actual completion of the international search

4 October 1996

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

International Application No

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A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08F220/22 C08G61/04 C07C251/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 208 309 A (MCDANIEL MAX P ET AL) 4 May 1993 see claims	1,2,4,5, 366, 384-415, 421,422, 426-438, 539-544, 560-562
A	GB 2 058 094 A (NIPPON OIL CO LTD) 8 April 1981 see claims	1,2,4,5, 366, 384-415, 421,422, 426-438, 539-544, 560-562

☒ Further documents are listed in the continuation of box C.

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INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US96/01282

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A	EP 0 361 363 A (PHILLIPS PETROLEUM CO) 4 April 1990 see page 5; claims ---	403,513, 519
A	WO 94 12699 A (EXXON CHEMICAL PATENTS INC) 9 June 1994 see claims ---	366,414, 511,517, 543
A	EP 0 378 248 A (STUDIENGESELLSCHAFT KOHLE MBH) 18 July 1990 see the whole document ---	496-501
A	EP 0 475 307 A (REXENE PROD CO) 18 March 1992 see the whole document ---	343,344
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X	JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, vol. 88, no. 22, 20 November 1966, WASHINGTON, XP002004034 SAITO, T. ET AL.: "Diethyldipyridylnickel. Preparation, Characterization, and Reactions" see page 5198 - page 5201 ---	243-247

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X	MACROMOLECULAR RAPID COMMUNICATIONS, vol. 16, no. 1, January 1995, HEIDELBERG, XP002004035 BARTOLINI, S. ET AL: "Enantioselective isotactic alternating copolymerization of styrene and 4-methylstyrene with carbon monoxide catalyzed by a cationic bioxazoline Pd(II) complex" see page 9 - page 14 ---	275-279
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X	MACROMOLUCULES, vol. 27, no. 10, 9 May 1994, WASHINGTON, pages 2694-2700, XP002003921 JIANG, Z. ET AL: "Stereo- and Enantioselective Alternating Copolymerization of alpha-Olefins with Carbon Monoxide. Synthesis of Chiral Polymers" see page 2696 ---	334-338
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INTERNATIONAL SEARCH REPORT

International Application No.

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C(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JOURNAL OF MOLECULAR CATALYSTS, vol. 35, no. 3, June 1986, LAUSANNE, XP002003923 TOM DIECK ET AL.: "Diazadienes as Control Ligands in Catalysis Part 12* The Nickel Catalyzed Cyclotetramerization of Propargylic Alcohol to Substituted Cyclooctatetraenes and the Structure of 1,3,5,7-Tetrakis(hydroxymethyl)cyclooctate traene" see page 317 - page 328 ---	243-266
X	EP 0 193 202 A (DU PONT) 3 September 1986	31-35
Y	see claims; examples 10,11 ---	31-36
Y	US 4 123 602 A (UKIHASHI HIROSHI ET AL) 31 October 1978 see the whole document ---	31-35
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X	EP 0 504 418 A (IDEMITSU KOSAN CO) 23 September 1992	345
A	see page 3, line 32; claims; examples 1,2,6,11 see page 12, line 7 see page 14, line 56 ---	346-357, 360-365, 510-527
X	EP 0 304 671 A (HOECHST AG) 1 March 1989	345-357
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X	US 3 505 301 A (NATTA GIULIO ET AL) 7 April 1970 see examples ---	361-363
X	DATABASE WPI Section Ch, Week 9428 Derwent Publications Ltd., London, GB; Class A18, AN 94-231215 XP002015135 & JP 06 168 625 A (NIPPON ZEON KK) , 14 June 1994	360-363
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INTERNATIONAL SEARCH REPORT

Intern: al Application No

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CHEMICAL ABSTRACTS, vol. 77, no. 8, 21 August 1972 Columbus, Ohio, US; abstract no. 49803, "MONTECATINI" SOCIETA GENERALE PER L'INDUSTRIA MINERIA E CHIMICA: "Catalytic manufacture of olefin copolymers with three or more monomer components" XP002015133	361-363, 520
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A	MACROMOLECULES, vol. 25, no. 1, January 1992, WASHINGTON, XP002015130 COLLINS, S. , KELLY, W.M.: "The Microstructure of Poly(cyclopentene) Produced by Polymerization of Cyclopentene with Homogeneous Ziegler-Natta Catalysts" see page 233 - page 237	345-357, 366-365

X	US 3 927 137 A (BRYSON JAY G) 16 December 1975 see the whole document	239,240

X	DE 39 06 434 A (HOECHST AG) 6 September 1990 see page 3, line 34 - page 4, line 43; claims	239,240

X	CHEMICAL ABSTRACTS, vol. 121, no. 11, 12 September 1994 Columbus, Ohio, US; abstract no. 134322, WISSING, E ET AL.: "Influence of bulky substituents on the regioselective group-transfer reactions of diorganozinc compounds with N,N'-bis(2,6-di-isopropenyl)-1,4-diaza-1,3 -butadiene" XP002015134 see abstract & INORG. CHIM. ACTA, vol. 220, no. 1-2, 1994, pages 55-61,	239,240

X	JOURNAL OF ORGANOMETALLIC CHEMISTRY, LAUSANNE, XP002015131 MUNZ, C., STEPHAN, C., TOM DIECK, H.: "Diazadiene-stabilized palladacyclopent-2-enes and the catalytic addition of various allylic systems to dimethyl acetylenedicarboxylate" see page 413 - page 422	239,240, 243-247

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INTERNATIONAL SEARCH REPORT

Internat. Application No.

PCT/US 96/01282

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	ZEITSCHRIFT FÜR NATURFORSCHUNG, vol. 45b, - 1990 TÜBINGEN, XP002015132 BONRATH, W. ET AL.: "Synthese und Struktur von Ni(2,6-iPr ₂ C ₆ H ₃ N=CH-CH=NC ₆ H ₃ -2,6-iPr ₂) ₂ " see page 1647 - page 1650 -----	239,240, 243-252

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 96/01282

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 395
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
Claim 395 is a product claim and refers back to claim 14, which is a process claim

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

SEE FURTHER INFORMATION SHEET

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☒ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/210

1. Claims : 1-25, 37-238, 243-344, 358, 359, 366 as far as they relate to claims 358, 367-394, 396-509, 510-520 and 523-527 as far as they relate to claims 358, 528-552, 554-562.
2. Claims : 26-36
3. Claims : 239-242
4. Claims : 345-357, 360-365, 366 as far as they relate to all mentioned claims except 358, 510-527.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 96/01282

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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